A New Method for the Determination of Wax Content of Crude Oils

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Abstract

This paper describes the development of a new method for determining the wax content in crude oils. Saturate fractions, obtained during hydrocarbon group separations by open column chromatography, were analyzed by gas chromatography with flame ionization detection (GC/FID). The GC used was a simulated distillation analyzer, equipped with a high-temperature (aluminum clad) column. The resulting chromatogram was integrated first to obtain the total area, and a second time to obtain the resolved C_{18}+ area. The ratio of the resolved area to the total area was then used to calculate the wax content of the oil.

Twenty-five different crude oils were analyzed using both the new method, and the conventional method of gravimetric determination of solvent-precipitated waxes. Overall, very good agreement was found between the two methods. Only three of the twenty-five oils tested had large differences between the GC and gravimetric was contents.

To confirm that coprecipitation of polar compounds could account for some or all of the observed discrepancies, one solvent-precipitated wax sample was subjected to a cleanup procedure (filtration through silica). N-alkane distributions from C_8 to C_{41} were obtained for the "clean" and "dirty" wax samples, the saturate fraction of the same oil, and a reference paraffin sample.

A significant increase in the n-alkane content of the cleaned wax, compared to the uncleaned sample, and the presence of n-alkanes in the C_8 to C_{17} range, support the conclusion that coprecipitation of polar compounds and entrapment of oil during wax crystallization can cause the gravimetric wax contents of some oils to be exaggerated. It is suggested that the most problematic oils are those that exhibit non-Newtonian flow behaviour at 15 °C.

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1.0 Introduction

Petroleum waxes are of two general types: paraffin or macrocrystalline waxes, in petroleum distillates, and microcrystalline waxes in petroleum residua (Speight, 1991). Paraffin waxes are composed primarily of straight-chain saturated hydrocarbons with 18 to 36 carbon atoms. Microcrystalline waxes contain a large percentage of branched and cyclic hydrocarbons with carbon numbers in the 30 to 60 range (Mansoori, 1996).

In the oil industry, waxy crude oils cause a variety of problems associated with deposition of wax in production equipment and pipelines. In downstream processes, dewaxing is a critical step in the production of high quality lubricating oils.

In the environment, the effects of weathering and low ambient temperatures produce dramatic changes in the rheological properties of even moderately waxy crude oils. This in turn significantly affects other oil properties such as evaporation and dispersibility. Hence, accurate determination of the wax content of crude oils is important.

Currently, the most commonly used method for the determination of waxes in crude oils, is precipitation from cold ketone solvent mixtures, followed by the gravimetric determination of the recovered waxes. However, the coprecipitation of polar material with the waxes, and the trapping of lighter hydrocarbon components, tend to exaggerate wax content, especially with heavier oils (Ronningsen and Bjorndal, 1991).

This paper describes the development of a new method for determining the wax content in crude oils by the gas chromatographic analysis of saturate fractions collected from hydrocarbon group separations. To confirm that coprecipitation of polar compounds can be a major source of error in the gravimetric determination of waxes, a cleanup was performed on one wax sample, and detailed analyses were made of both the "clean" and "dirty" wax.

2.0 Methods

2.1 Determination of Wax Content

2.1.1 Gravimetric Method

Details of this method have been described previously (Jokuty *et al.*, 1994). In summary: After removal of asphaltenes by precipitation and filtration from n-pentane, waxes are precipitated from the deasphaltened oil (maltenes) with a methylene chloride/methylethyl ketone mixture, at –30 °C. The precipitated waxes are filtered from the cold solution, dryed, and weighed. Samples are run in duplicate and the wax content is calculated as the average of the weight percents of precipitated wax to oil.

2.1.2 Gas Chromatographic Method

The saturate fraction of a crude oil is obtained by hydrocarbon group separation, described briefly as follows. After removal of asphaltenes by precipitation and filtration from n-pentane, the maltenes are separated on an open silica column, into saturates, aromatics, and resins by sequential elution with hexane, hexane/benzene, methanol, and methylene chloride (Jokuty *et al.*, 1995).

Light ends, lost during solvent recovery, are calculated as the difference between the maltenes expected (100% – asphaltenes), and the maltenes actually recovered. The weight percents of saturates, aromatics, and resins are calculated by making the reasonable assumptions that a) resin and asphaltene contents are not affected by evaporative losses, and b) the aromatic portion of the light ends can be equated to the benzene, toluene, ethylbenzene, xylenes, and C_3-substituted benzenes (BTEX + C_3-benzenes) content of the crude oil (Wang *et al.*, 1995). The remainder of the light ends, calculated by difference, are referred to as the low-boiling saturates (LBS). The saturates recovered from the column are referred to as the high-boiling saturates (HBS). The HBS sample is prepared and run as for simulated distillation

(SIMDIS) (Jokuty *et al.*, 1996). The SIMDIS analyzer uses a special high-temperature column and is capable of resolving n-alkanes from C_5 to C_{120}.

The chromatogram obtained is analyzed using HP ChemStation software (Hewlett-Packard Co., U.S.A.). The chromatogram is integrated once, to obtain the total area, and a second time, manually, to obtain the area of the resolved peaks, beginning at a retention time corresponding to that of n-octadecane (n-C_{18}), as determined from the analysis of a calibration mixture containing n-alkanes from C_5 to C_{120}. Figures 1 and 2 show the chromatogram of Arabian Medium saturates integrated both ways.

To calculate the wax content of an oil, first the HBS content is calculated.

$$\text{HBS \%} = 100 \times \frac{\text{HBS}_{\text{recovered}}}{\text{maltenes}_{\text{used}}} \times \frac{\text{maltenes}_{\text{recovered}}}{\text{oil}_{\text{used}}} \times \frac{(\text{saturates} + \text{aromatics})_{\text{expected}}}{(\text{saturates} + \text{aromatics})_{\text{recovered}}}$$

Then the wax content is calculated by multiplying the HBS % by the ratio of the area of the resolved C_{18}+ portion of the chromatogram to the total area. A sample calculation for Arabian Medium crude oil follows.

HBS = 35 g/100 g oil
Resolved C_{18}+ area = 7,220,246
Total area = 36,900,015
Ratio = 0.20 g wax/g HBS
Wax content of oil = (0.20 x 35) = 7 g/100 g oil = 7 wt %

2.2 Wax Cleanup Method

The wax cleanup method was based on a method described in Ronningsen and Bjorndal, 1991. It was found, however, that larger solvent volumes were required to dissolve the Sumatran Light wax sample.

a) Wax recovered as described in 2.1.1 (~0.8 g) was dissolved in 100 mL of toluene.
b) The dissolved wax was filtered through a nylon filter membrane (0.45 μm pore size) to remove remnants of glass microfibre filter.
c) The filtrate was transferred to a pre-weighed beaker and blown down with compressed air to remove the toluene.
d) The recovered wax (~0.7 g) was dissolved in 20 mL of hexane.
e) The wax solution was filtered through a short column made from a 5-cc glass syringe, filled with silica to the 3-cc mark. Glass wool was used to retain the silica in the syringe.
f) The filtrate was transferred to a pre-weighed beaker and blown down with compressed air to remove the hexane.
g) The cleaned wax was air-dried overnight, and then weighed.

2.3 GC/FID and GC/MS Analysis of Saturate Fractions and Waxes

a) Saturate samples were weighed and dissolved in hexane. Wax samples were weighed and dissolved in toluene. All samples were made up to 5.00 mL.
b) A 900-μL aliquot of each sample solution was spiked with 100 μL of 200-ppm internal standard (5-α-androstane).
c) GC/FID and GC/MS analyses were performed as described in Wang *et al.*, 1994.

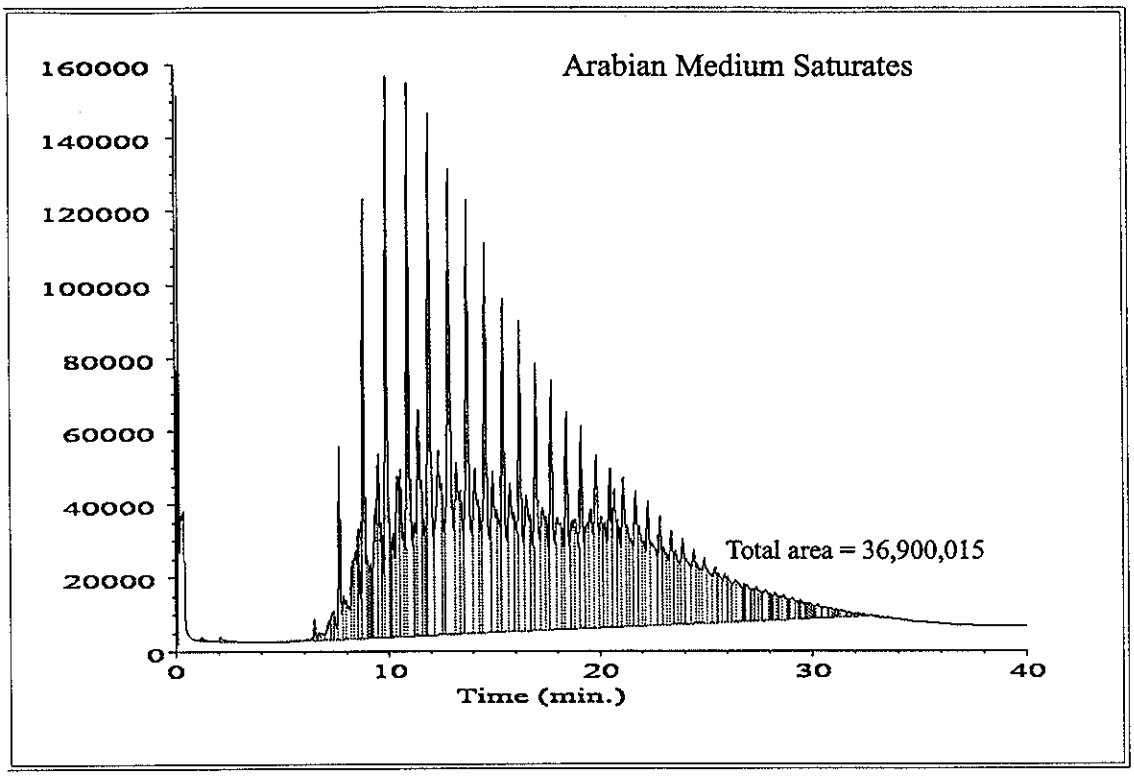

Figure 1. Total Area Integration

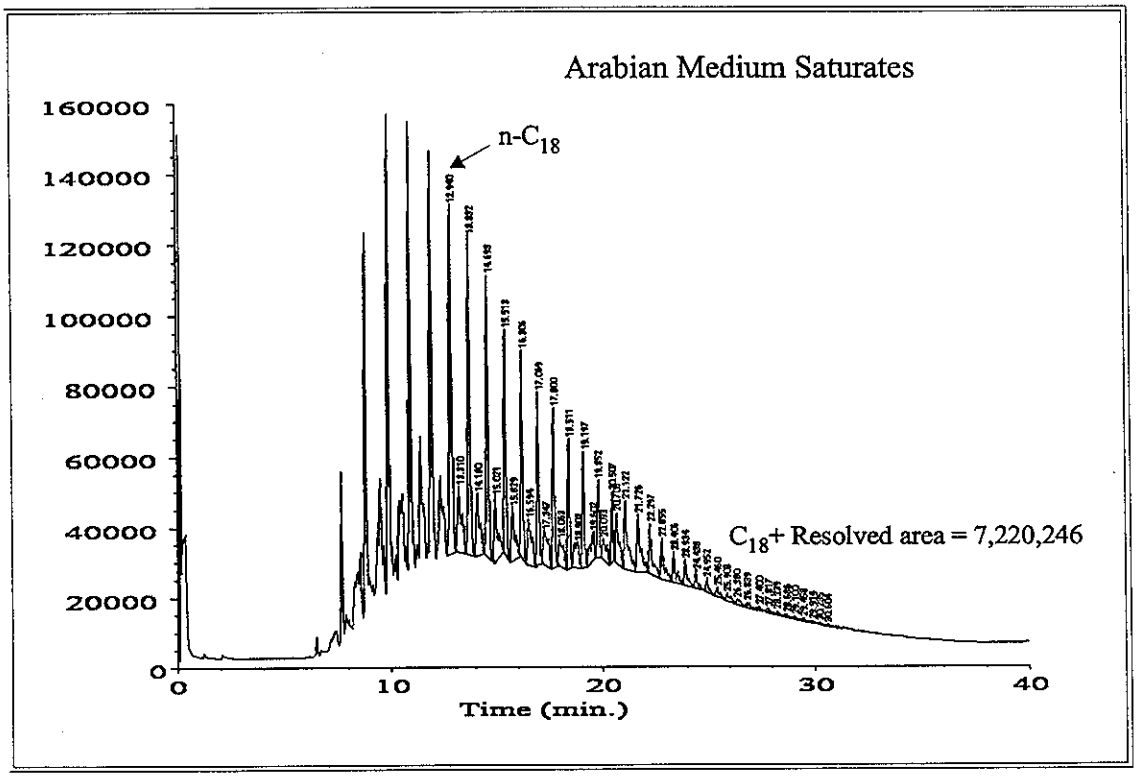

Figure 2. Resolved Area Integration (C_{18}+)

3.0 Results

Both the gravimetric method and the GC method were used to determine the wax contents of 25 crude oils. The results for each oil are presented in Table 1. A "delta" value, the difference between the two wax contents, is also included in Table 1, as are hydrocarbon groups, density, viscosity, and pour point, for each oil.

The range of GC wax values was 1% to 24%. The range of gravimetric wax values was 1% to 37%. Delta values ranged from –17 to +2, with 80% falling between –2 and +2 inclusive.

To determine the extent to which coprecipitation of polar compounds might occur when using the gravimetric method, one of the duplicate wax samples recovered from Sumatran Light crude oil was subjected to the wax cleanup described in 2.2. The "clean" and the "dirty" wax were then analyzed by GC/FID and GC/MS to determine the n-alkane distribution in the C_8 to C_{41} range. In addition, the Sumatran Light saturate sample, and a sample of the paraffin wax used as a standard during the development of the gravimetric method, were also analyzed. The alkane distributions for all four samples are presented in Table 2.

4.0 Discussion

Overall, the results from the new method compare very well with those from the old gravimetric method. Twenty of the 25 oils listed in Table 1 show excellent agreement (delta between –2 and +2) between their two wax contents. Of the remaining five oils, two (Rangely and Malongo) have wax contents that are in good agreement, with delta values of –5 and –3 respectively. Three oils (Taching, Sumatran Light, and Sumatran Heavy) have GC wax contents much lower than gravimetric wax contents, with delta values of –9, –13, and –17 respectively. To understand why the GC and gravimetric wax contents differ so much for these three oils, it is helpful to look at some of their chemical and physical properties.

Taching and Sumatran Light both have GC wax contents of 24%, compared to gravimetric wax contents of 33% and 37% respectively. Clearly, these are very waxy oils. This is reflected in their very high pour points (38 °C). It should be noted, however, that Sumatran Light is lighter than Taching, as measured by their densities of 0.8600 g/mL and 0.8700 g/mL respectively. Low-boiling saturates are absent in Taching, but make up 8% of Sumatran Light. As shown in Table 2, in the Sumatran Light wax samples, alkanes lighter than C_{18} accounted for 5% of the total n-alkanes found in the "dirty" wax, but only 1% in the "clean" wax. Also, cleaning the wax resulted in a 35% increase in the n-alkane content, from 368 mg/g to 497 mg/g, indicating the removal of non-alkane material. In view of this evidence, the delta value of –9 for Taching is probably due solely to coprecipitation of resins (9%), while the delta value of –13 for Sumatran Light is likely due to a combination of coprecipitation of resins (6%) and entrapment of oil during wax crystallization.

Sumatran Heavy has a GC wax content of 7% but a gravimetric wax content of 24%. Figures 3 and 4 show the extreme difference in the amount of resolved material in the saturate fractions of Sumatran Heavy and Sumatran Light. Clearly, Sumatran Heavy is much less waxy than Sumatran Light. This is confirmed by a much lower pour point for Sumatran Heavy, 18 °C, compared to 38 °C for Sumatran Light. Taking into account that the total saturate content of Sumatran Heavy is 46% compared to 70% for Sumatran Light, that low-boiling saturates are absent in the former oil, but make up 8% of the latter, and that the resin content of Sumatran

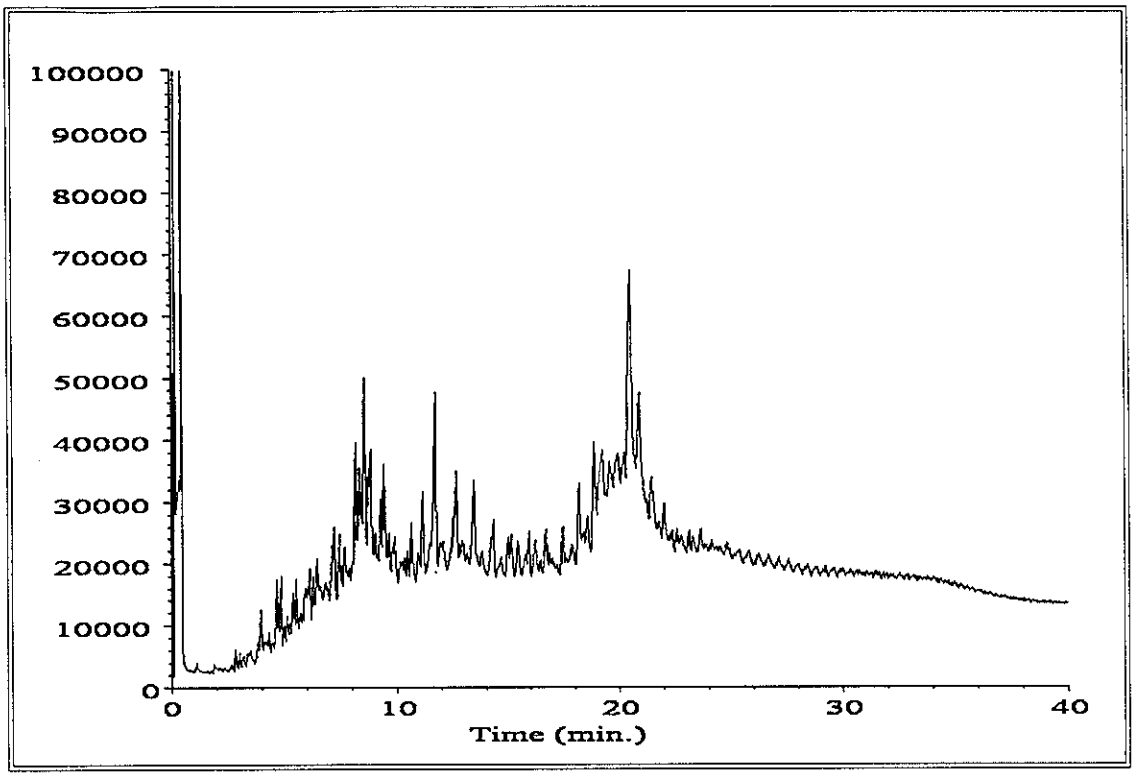

Figure 3. Chromatogram of Sumatran Heavy Saturates

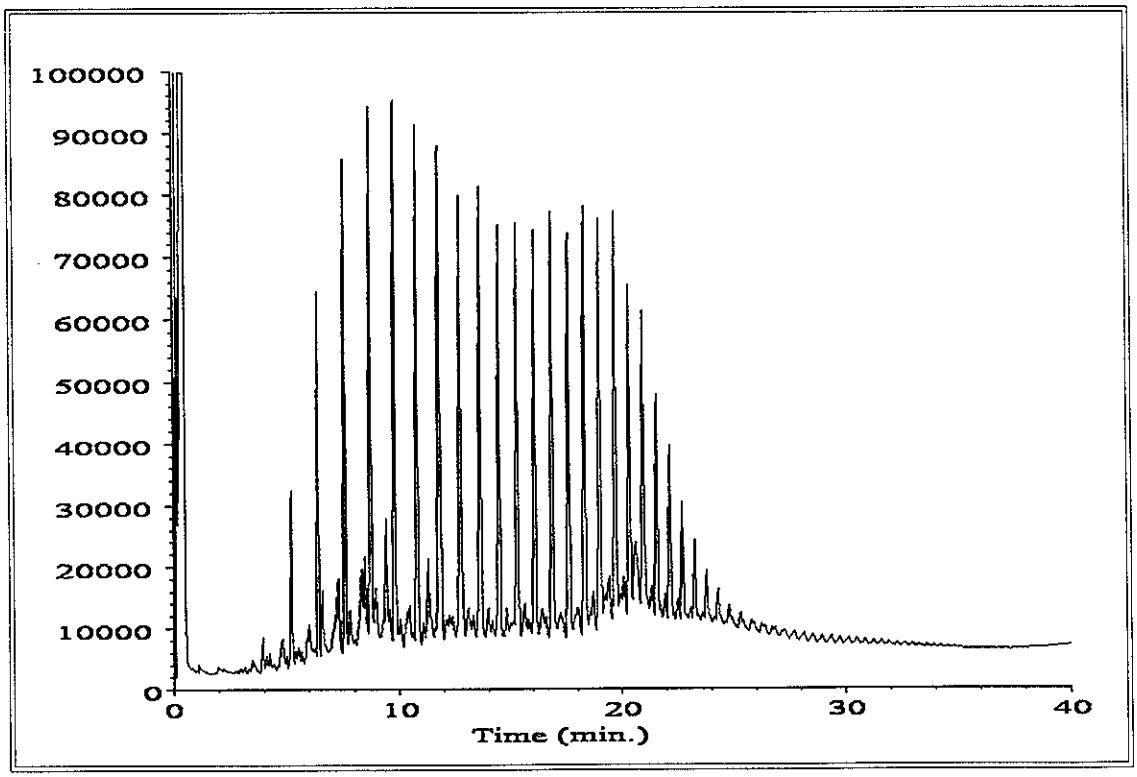

Figure 4. Chromatogram of Sumatran Light Saturates

Table 1. Wax Contents and Other Properties of Various Crude Oils

Oil Name	Density @ 15 °C (g/mL)	Viscosity @ 15 °C (mPa·s)	Pour Point (°C)	Saturates (wt %)	Low Boiling Saturates (wt %)	High Boiling Saturates (wt %)	Aromatics (wt %)	Resins (wt %)	Asphaltenes (wt %)	GC Waxes (wt %)	Grav. Waxes (wt %)	Delta*
Gullfaks	0.8701	13	-32	60	13	47	35	5	1	4	2	2
Arabian Light	0.8658	14	-28	51	12	39	39	6	3	6	4	2
Iranian Heavy	0.8756	20	-22	53	18	35	30	11	6	6	4	2
Eugene Island Block 43	0.8404	13	0	81	14	67	16	3	1	9	7	2
Main Pass Block 306	0.8606	9	-53	65	17	48	29	5	1	2	1	1
Louisiana	0.8518	8	-28	73	17	56	21	4	1	4	3	1
Federated	0.8783	4	-15	74	28	46	21	3	1	7	6	1
Arabian Medium	0.8293	29	-10	54	19	35	32	7	6	7	6	1
Komineft	0.8408	13	12	70	21	49	22	6	2	8	7	1
Terra Nova (1994)	0.8457	11	5	62	16	46	31	6	2	10	9	1
Atkinson	0.9110	65	-45	48	10	38	36	14	3	1	1	0
Green Canyon Block 109	0.8921	39	-36	51	13	38	39	9	1	2	2	0
Oseberg	0.8522	10	-9	65	22	43	25	8	2	5	5	0
Sockeye	0.8965	45	-12	48	14	34	31	13	8	5	5	0
Point Arguello Light	0.8739	22	-22	57	17	40	27	9	7	7	7	0
Brent	0.8351	6	-6	72	26	46	23	4	1	8	8	0
Statfjord	0.8354	6	-2	68	20	48	26	6	2	8	8	0
IFO 180	0.9670	2,324	-10	29	1	28	51	11	10	7	8	-1
California (API 15)	0.9770	6,400	-9	19	5	15	35	23	22	1	3	-2
Hondo	0.9356	735	-15	33	12	21	31	24	12	4	6	-2
Malongo	0.8701	63	21	62	13	49	25	9	4	11	14	-3
Rangely	0.8567	33	17	71	17	54	21	5	4	9	14	-5
Taching**	0.8700	5,138,000	38	74	0	74	12	9	6	24	33	-9
Sumatran Light***	0.8600	322,800	38	70	8	62	15	6	8	24	37	-13
Sumatran Heavy***	0.9312	117,500	18	46	0	46	30	13	10	7	24	-17

*Delta = GC wax - Grav. wax **shear rate for viscosity measurement = 0.1/s ***shear rate for viscosity measurement = 1/s

Table 2. n-Alkanes in Various Saturate Fractions and Waxes

n-Alkanes (mg/g)	Sumatran Lt. Saturates	Sumatran Lt. Dirty Wax	Sumatran Lt. Clean Wax	Paraffin Wax
C_8				
C_9		3.85		
C_{10}	0.37	0.65		
C_{11}	2.22	0.59		
C_{12}	4.95	1.21		
C_{13}	7.19	1.90	0.08	
C_{14}	8.58	2.58	0.53	
C_{15}	9.24	2.99	1.28	
C_{16}	9.19	3.25	1.97	
C_{17}	9.90	1.87	1.34	
C_{18}	8.56	2.17	1.72	
C_{19}	7.81	8.08	10.00	0.23
C_{20}	7.80	11.48	16.91	0.68
C_{21}	8.22	17.91	26.99	5.52
C_{22}	8.39	22.26	34.04	22.46
C_{23}	8.97	26.69	40.94	53.21
C_{24}	8.97	28.42	42.92	85.95
C_{25}	9.28	30.87	45.53	101.93
C_{26}	9.51	32.05	45.69	107.74
C_{27}	9.87	33.90	47.14	101.44
C_{28}	8.16	28.62	38.97	85.64
C_{29}	7.46	27.57	37.19	81.61
C_{30}	5.40	21.96	29.40	53.39
C_{31}	4.27	16.96	21.96	43.50
C_{32}	3.03	12.66	16.48	29.55
C_{33}	2.29	9.34	12.21	19.56
C_{34}	1.39	6.33	8.30	12.58
C_{35}	0.97	4.38	5.80	8.36
C_{36}	0.69	2.42	3.18	5.41
C_{37}	0.33	1.67	2.11	3.58
C_{38}	0.23	1.21	1.57	2.65
C_{39}	0.12	0.90	1.24	1.83
C_{40}	0.12	0.74	0.76	1.46
C_{41}	0.10	0.40	0.50	1.01
$<C_{18}$	52	19	5	0
$C_{18}+$	122	349	492	829
Total	174	368	497	829
% $<C_{18}$	30%	5%	1%	0%
% $C_{18}+$	70%	95%	99%	100%

Heavy (13%) is more than twice that of Sumatran Light (6%), it is probable that the large discrepancy between the GC and gravimetric wax values for Sumatran Heavy (delta = –17) is due primarily to coprecipitation of resins and entrapment of oil during wax crystallization.

5.0 Conclusions

The new GC method for determining the wax content of crude oils works very well. For most oils, the GC wax content and the gravimetric wax content are comparable. If hydrocarbon groups and BTEX + C_3-benzenes data are not needed, or cannot be determined, the gravimetric method will generally produce an acceptable result. However, for some oils, notably those with non-Newtonian flow behaviour at 15 °C, as determined by viscosity measurements, the GC method gives a more accurate value. This could be an important consideration when determining wax content of weathered crude oils, as many oils exhibit non-Newtonian flow behaviour after moderate evaporative losses.

Future wax content determinations by the Emergencies Science Division will be done by the GC method. The primary reason for changing to this method is the reduction in time, effort, and cost to produce the wax content data. The saturate fractions are collected from the hydrocarbon groups separation in any case. In 30 minutes, 10 samples can be prepared for automated GC analysis, which will be complete within 16 hours. Subsequent data analysis will require approximately 2 hours, for a total analysis time of less than 24 hours. In contrast, it requires 3 days to analyze 2 oils in duplicate using the gravimetric method.

6.0 Acknowledgements

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